USGS Methods: Water, Sediment and Colloids

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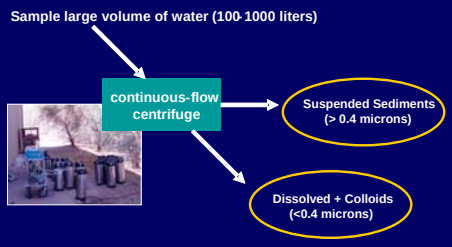
Overview of Methods

- Water
  - Separation of fractions
  - Dissolved
  - Suspended sediments
  - Sorption to containers
- Sediments
  - Bed and suspended sediments
- Colloids
  - SPME

Pyrethroids Included

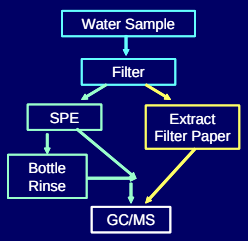
- Allethrin
- Bifenthrin
- Cyfluthrin
- Cyhalothrin
- Cypermethrin
- Deltamethrin
- Esfenvalerate
- Fenpropathrin
- Fluvalinate
- Permethrin
- Resmethrin
- Sumithrin (Phenothrin)
- Tetramethrin

Separation of Sample



Water Method

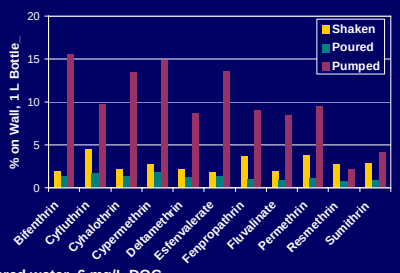
- 1-L sample
- Filter (0.7 µm glass fiber)
- Solid Phase Extraction (HLB cartridge)
- Bottle rinse (sorbed pyrethroids)
- Extract filter paper (suspended sediments)
- GC/MS and GC/MS/MS (ion-trap)
- Recovery 91-98%
- MDLs 2-5 ng/L



Pyrethroid Sorption

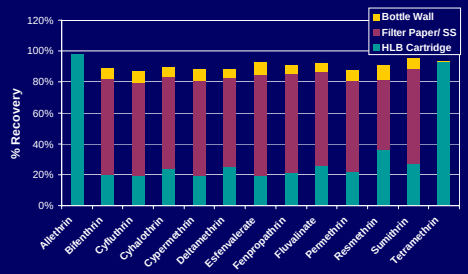
- Pyrethroids in water sorb to sampling containers (glass or plastic)
  - Up to 50%
  - Analytical and toxicological importance
- Composition of sample influences extent of sorption
  - DOC
  - Suspended sediments
  - Relative surface area of container

Container Sorption- Varying Removal



- Filtered water, 6 mg/L DOC,
- Equilibrated for 24 hours
- Spiked at 200 ng/L

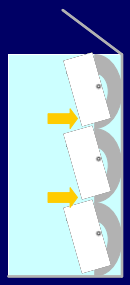
Water Mass Balance



- Unfiltered water, 5 mg/L DOC, 13.9 mg/L SSC,
- Equilibrated for 3 days
- Spiked at 400 ng/L

Pyrethroid Sorption to Containers

- Not all pyrethroids sorb to the same degree
- Allethrin and tetramethrin sorb less →lack similar functional group
- Sorption seems to be "loose association"



Sorption- Additional Work

- Sorption addressed for analytical purposes not for toxicity or sampling
  - Continue exploring ways to mitigate or address pyrethroid sorption
  - Need concentration organisms are exposed to
- EPA funding to develop SOP for water sampling (FY07-08)
  - Cross-sections, composite samples
  - Autosamplers

Pyrethroid Water Method- SPE Storage

- SPE cartridge storage
  - Dried
  - Put in freezer
- Tested HLB and C8
  - Found not degradation on either cartridge after 1 month
- Can store cartridges

Sediment Method

- 5-10 g samples
- MASE extraction at 120 ºC, 50 % moisture with DCM:Methanol (9:1)
- Matrix clean-up: Carbon/Alumina stacked cartridges
  - Eluted with DCM
- Sulfur clean-up: GPC or activated Cu
- GC/MS or MS/MS
- Recovery 80-93%
- MDLs 1-5 ng/g

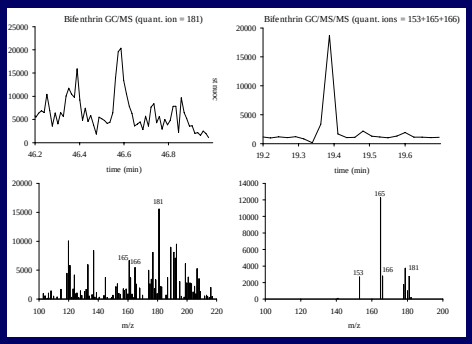
Sediment Method Development

- MASE temperature
  - Did not achieve complete extraction with 100 ºC
- MASE solvent
  - Started with 1:1 DCM:Acetone
  - More efficient (less matrix) with DCM;Methanol
- Clean-up
  - Tried 10 g Florisil
  - No significant reduction of matrix and more time consuming
  - Also took other current use pesticides into consideration

GC/MS

- Instrument
  - Varian
    - 3800 GC
    - Saturn 2000 MS (ion-trap)
- Column
  - DB-5MS
    - 30 m × 0.25 mm × 0.25 µm
- Individual isomer peaks added; reported as total compound
- GC/MS/MS
  - Increases confirmation by decreasing background
  - Does not significantly reduce MDLs

GC-MS/MS



MDL Limitations

- Instrument (ion-trap) is at sensitivity limit
- Sediment samples have more matrix problems
  - Greater concern for multiple isomers
- Cannot increase sample size (suspended sediments)

Colloids- Separation

Sample large volume of water (100-1000 liters)

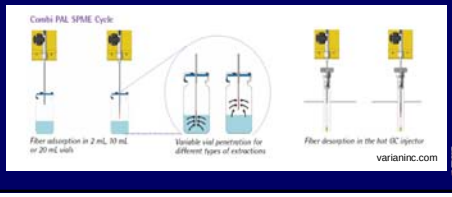
continuous-flow centrifuge → Suspended Sediments (> 0.4 microns)

tangential-flow ultrafilter → Colloids (between 1000 Daltons and 0.4 microns)

"truly dissolved" (< 1000 Daltons)

SPME

- Solid-phase microextraction
- Fused silica fiber coated with appropriate stationary phase
- Used to measure total and bioavailable compounds



Colloids- Measurement of Pyrethroids

- Several types of SPME
  - Headspace, liquid
- Negligible depletion SPME
  - Freely dissolved (or bioavailable) fractions
  - Only if equilibrium is not disturbed (EE of less than 5-10%)
  - Sample matrix should not disturb sorption kinetics

SPME- Parameters

- 20 mL of water
- Fiber
  - Tested 7 and 100 μm PDMS phase
  - 1 cm
- Total pyrethroids
  - Sorption onto fiber at 90 ºC for 30 min with agitation
  - Desorption at 275 ºC for 3 min
- Negligible depletion/ Bioavailable
  - Based on Liu et al., 2004, ET&C, 23, p 7-11.
  - Sorption at ambient temperature for 10 min with agitation
  - Desorption at 275 ºC for 3 min